REDUCTION OF HAZARDOUS WASTE METALS SLUDGE AT HILL AIR FORCE BASE

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INTRODUCTION

Reduction of hazardous waste generation and disposal is an ongoing primary goal at Hill Air Force Base. It has been a major focus of the hazardous waste management program since 1985 and Slide 4 shows the results of those efforts through 1997. Note that a significant portion of the disposal is identified as Industrial Wastewater Treatment Plant (IWTP) sludge. This sludge has been disposed as a hazardous waste because it is a listed waste, number F006, wastewater treatment sludges from electroplating operations. It is listed due to the hazardous constituents; cadmium, hexavalent chromium, nickel, and cyanide (complexed). The sludge is also considered a hazardous waste because it often fails the TCLP procedure for cadmium and chromium and is, therefore, a characteristic hazardous waste with the waste numbers D006 and D007.

It was apparent early last year that in order to meet the hazardous waste reduction goal for 1999 it would be necessary to reduce the sludge production and disposal. Therefore, a project was organized to accomplish this and the following major pieces were defined.

- Improve process control to reduce water content
- Regulations review to evaluate applicability of F006 waste number
- Establish a mass balance for cadmium and chromium
- Research practices at other similar shops
- Separate non-reactive solids into separate waste stream
- Reduce input of cadmium and chromium from the cleaning and electroplating shops

This paper describes a project that has accomplished a reduction of the cadmium and chromium input from the cleaning and electroplating shops to the main IWTP process and the consequent reduction in the production of the final hazardous waste sludge. The objective was to evaluate and test the feasibility of separation of the heavy metals, chromium and cadmium, in the pretreatment module of the IWTP rather than introducing them directly into the main plant flow. The desired result was reduction of the inflow of these two heavy metals into the IWTP equalization tanks to values as low as technically and economically feasible.

BACKGROUND

The industrial wastewater collection system at Hill Air Force Base includes:

- Wastes from metal finishing operations
- Wastes from electroplating operations
- Wastewater from washing of aircraft
- Wastewater from painting operations
- Backwash from the oil sorbent and activated carbon units
- Filtrate from the sludge dewatering facility
- Supernatant from the sludge holding tank
- Flight line washdown infiltration
- Stormwater flow
- Contaminated groundwater from on site remediation operations

The treatment plant is designed for an average flow rate of 400 gpm and a maximum flow rate of 600 gpm. It operates as a point source under a NPDES permit discharging to the local sewer district and must meet the Categorical Pretreatment Standards under 40 CFR 403.6. The effluent must meet standards for cyanide, pH, oil and grease, suspended solids, total toxic organics and a list of eleven metals including cadmium and chromium. These are the major metal contaminants that the process is designed to remove. This is accomplished by pH adjustment with sulfuric acid and addition of sulfur dioxide followed by addition of sodium hydroxide, which precipitates the heavy metals as oxides. These solids are then separated by flocculation, clarification, filtration and drying to become the hazardous waste sludge that is being disposed. A mass balance study was done last summer to provide better data on the sources of cadmium and chromium in the influent to the IWTP. Slide 5 shows the relative amounts and the flows in a simplified schematic. This study put some numbers to the already known fact that the major contributors were the electroplating and surface preparation processes in the landing gear maintenance operations of the Commodities Directorate. It also quantified the proportion of these two metals that were coming as concentrated waste solutions, in carboys, to the batch pretreatment process at the IWTP as compared to the mass coming in the continuous flows into the main portion of the plant.

APPROACH

The approach recognized that a significant portion of the total cadmium and chromium inflow from these major sources was first coming into the pretreatment process. If changes could be effected in the batch pretreatment to remove these two metals prior to entry into the main IWTP flow significant benefits appeared to be possible. It was also anticipated that if these two metals could be separated as high concentration solids it might be possible to reclaim the metal values by recycling or treatment. Past attempts to reclaim the metal values from the IWTP sludge were unsuccessful due to the very low concentrations of the metals in that sludge.

The project was defined to include the following:

- Assess and evaluate the current pre-treatment process for chromium and cadmium including data on flows and composition of flows.
- Provide a plan for obtaining the additional data needed and obtain the data.
- Install two filter units that had been obtained in anticipation of this use and test their capability to filter out the cadmium solids.
- Evaluate available precipitation and separation technologies for chromium and recommend changes to incorporate the best candidate in the pretreatment process.
- Utilize equipment and materials currently in use to the maximum extent feasible.
- Perform bench /pilot scale testing of the proposed process changes.
- Make changes to the pre-treatment process piping and equipment necessary to test the proposed changes while maintaining plant operation.
- Conduct testing, evaluation and demonstration of the process changes on site, train the IWTP operators, and transfer operations to them.
- Provide documentation including operation and maintenance manuals.
- Investigate recycle or treatment of the separated solids to reclaim the metal values.

At the beginning of the project Hill Air Force Base Environmental Management (EMC) and Radian International recognized the importance of forming a team with all of the significant stakeholders involved. The team included the people from the Commodities Directorate who generate the major proportion of the waste and the people at the IWTP who process the waste, including the engineer, supervisor and operators. Weekly teleconferences were held involving the affected stakeholders and interaction between project engineers and IWTP operations people was routine.

ASSESS CURRENT PROCESS

The pretreatment process is designed to treat and regulate the discharge of waste cyanide, cadmium, and chromium. These waste chemicals originate in metal stripping and plating operations occurring in Buildings 238, 505, and 507. Chemicals are transferred to one of five concrete tanks located outside the IWTP process building: two cyanide/cadmium treatment bays, one concentrated cyanide tank, one alkali tank, and one chromium tank. The tanks are depicted in slide 7 and slide 8.

A Wonderware control system is available to the operators who control (either automatically or manually) the treatment and discharge of the tanks to the main IWTP equalization/feed tanks. Slide 9 depicts one of the screens from the Wonderware system.

The process flow diagram for the cyanide/cadmium portion is shown in slide 10.

Low concentration discharge from the Building 505 plating shop cadmium rinse tanks, leakage, and wash-down wastewater, flow intermittently to a cyanide wet well. A liquid level switch triggers pumping in discrete batches from the cyanide wet well to one of the two cyanide/cadmium treatment bays. Flows vary depending on plating shop operations. Typically, they decrease during the night, on weekends, and during holidays. Data estimated from level measurements in the treatment tanks indicated a weekly flow of approximately 30,000 gallons. Cadmium concentration in the inflow from the wet well during July and August varied between 3 and 20 ppm with an average of 12.4 ppm.

Also, concentrated waste cyanide/cadmium solutions are delivered in carboys and transferred to the concentrated cyanide tank. The quantity is low, averaging 833 gallons annually. Cadmium concentration is much higher and is estimated at 2.5% by weight based on data for 1996. A pump is used to periodically transfer this concentrated solution into the cyanide/cadmium treatment bay in roughly one-inch intervals (approximately 100 gallons). The level of the concentrated tank and operator judgment determines how frequently concentrated solution is added to the cyanide/cadmium treatment bay.

The two cyanide/cadmium treatment bays are rated at 10,000 gallon capacity each. The entering solutions contain complex metallic cyanides, primarily cadmium cyanide. Cadmium cyanide complexes dissociate almost totally in very dilute solutions to form free cyanide. At the pH of most natural waters, the free cyanide exists as molecular HCN, which is very toxic. When a cyanide/cadmium treatment bay is filled, chlorine and sodium hydroxide are added until the pH is greater than 9 and the ORP (oxidation-reduction potential) is above 300. At these levels, most of the CN group is present as the cyanide ion CN^-. While the batch treatment system is automated, operators routinely check pH and ORP to ensure that proper treatment is obtained.

After the reactions have neutralized the cyanide and formed the cadmium containing solids the reacted mixture is pumped to the IWTP equalization/feed tanks. No attempt had previously been made to separate the cadmium containing solids. In fact the solids are re-dissolved when the sulfuric acid is added to adjust the pH prior to further treatment.

Concentrated acidic solutions, principally chromic acid, are delivered in carboys and transferred to the chromium tank. Quantities are considerably larger than the cadmium solutions at 19,500 gallons per year. Chromium concentration of these solutions varies widely. As an example, in 1996 the mass of total chromium was 5,584 pounds which is a concentration of approximately 3.2% by weight. Previously, these solutions were periodically transferred to the IWTP equalization/feed tanks at slow rates without further treatment.

Concentrated high pH solutions are delivered in batches by carboys to the alkali tank These solutions are transferred from chemical milling, alkaline etching, nickel, cadmium, and aluminum stripping, cadmium plating, and rust stripping processes. Hence, added carboy chemicals include sodium hydroxide, sodium carbonate, sodium cyanide, cadmium oxide, aluminum, and tri-sodium phosphate. This solution is slowly added to the IWTP equalization/feed tanks.

PLAN TO OBTAIN ADDITIONAL DATA

The process assessment indicated the gaps in and weaknesses in the flow and concentration data for the pretreatment process. The additional data needs were identified as:

- Flow meter for cyanide wet well
- Influent concentration of cadmium to treatment tank
- Cadmium concentration in treatment tank after addition of carboy solution.
- Chromium concentration in the tank prior to treatment

It was anticipated that concentration data both upstream and downstream of the proposed filter presses would be needed in order to evaluate the removal efficiency.

INSTALL AND TEST FILTERS ON CADMIUM

Two small filter presses had been purchased in early 1997 in anticipation of this project. These were installed in June and July in the basement of IWTP building 10581 adjacent to the pretreatment tanks that are just through the wall to the west. The schematic layout is shown in slide 11. The presses are JWI units with 32 square feet of filter area, polypropylene plates and cloth , with opening size comparable to the opening size in the cloth your shirt is made of. Photos of the cadmium press and piping are slides 12 & 13. The pump is an All-flo, 1'' air operated double Teflon diaphragm, with adjustable capacity from 0-40 gpm. The piping is schedule 80 PVC.

The first filtering system was tested on the cadmium solution in July and August. Prior to the operation of the press the discharge time for a batch from the treatment tank was less than one hour or approx. 140 gpm. The discharge rate going through the press is approx. 6 gpm. The data on the press runs for the first 5 batches is shown in slide 14. The removal efficiency for the cadmium solid was 98% as shown on this slide with the cadmium content reduced from 13 ppm in the influent to 0.25 ppm in the effluent. One press drop was required for the first 27,000 gallons of filtrate. The press capacity is 1.5 cubic feet so 3 normal drops can be put in a 55-gallon open top drum. Slide 15 is a view of the open filter press with the filter cake on the cloth.

Slide 16 is a view of the cake going into the drum. Results of further testing in July, August and September are shown in slide17. In the later tests concentrated cadmium solutions were added and pH values were increased which improved removal effectiveness.
The filter cake(sludge) has no free liquid and is 45% solids. The solids consist of 31.5% calcium carbonate, 7.4% cadmium oxide, 4.2% magnesium carbonate and 1.9% all other metal oxides or hydroxides. Because of the high cadmium content the sludge can be recycled to reclaim the cadmium as will be discussed later. The test showed conclusively that 90+% of the cadmium being treated in the pretreatment process can be removed before it ever sees the IWTP main treatment process.

CHROMIUM SEPARATION EVALUATION, TESTING AND DEMONSTRATION

This part of the project was not as straight forward as the cadmium separation, which was already in the form of a precipitate and just had to be filtered. The chromium is in the form of a concentrated solution that must first be treated to form chromium containing solid and then the solid separated by filtration. The first step was to evaluate the existing processes for chromium reduction and precipitation and choose the one that made the most sense for implementation at Hill. One of the major factors in the decision was the capability to maximize the use of existing equipment, chemicals and personnel for the chosen process. Another significant factor was the ability to make the process equipment changes without disruption of the ongoing IWTP process.
Available technologies were screened and seven possible processes were listed. Two of these were selected for final evaluation, which included bench testing in the laboratory. The two final candidates were a) the conventional method, most widely used, which uses sulfur dioxide and sodium hydroxide, and b) the sulfide method which uses sodium sulfide and ferrous sulfate. Results of the bench tests showed that both methods achieved chromium removal above 99.99%. However, due to other factors the conventional method was chosen. The advantages of this method are summarized in slide18. The sulfide method has advantages also, but more disadvantages, which are summarized in slide 19. The conventional treatment method was clearly the choice.
The first step in the treatment is the reduction of hexavalent chrome to trivalent chrome, which occurs by the following first order chemical reaction:

$$3SO_2 + 2H_2CrO_4 + 3H_20 \text{ --> } Cr_2 (SO_4)_3 + 5H_2O$$

This reaction occurs as sulfur dioxide gas is diffused into the acidic concentrated chromium solution.
The second step is the formation of the solid chromium hydroxide by the following first order reaction with sodium hydroxide:

$$Cr_2(SO_4)_3 + NaOH \text{ --> } Cr_2(OH)_3 + Na2SO_4$$

Implementation of the treatment process required additional piping to add sulfur dioxide and sodium hydroxide to the existing concentrated chromium solution tank. Piping revisions were also made so that the processed solution could be filtered by the two filter presses. Also, a pump to deliver sodium hydroxide was installed. A schematic for the combined processes is shown in slide 20. A schematic layout is shown in previous slide 11.
The first reaction is initiated within the chrome tank, shown in slide 21, by opening the valves between a 1-ton sulfur dioxide (SO_2) cylinder stored in the cylinder room (main floor of Building 10581) and the chrome tank. Sulfur dioxide is added for several days until chrome reduction is complete, as indicated when ORP readings gradually change from around 800 or 900 mV to less than 460 mV (at pH less than 1) or less than 400 mV (at pH less than 1.5). This is confirmed by laboratory tests that hexavalent chrome is less than 1 ppm. The photo in slide 22 shows the batch near the end point. Once reduction is complete, the SO_2 valves are closed. Operators carefully monitor the cylinder weight, ORP levels, and any leakage of $SO_{2.}$
Now sodium hydroxide(caustic) is added to initiate the second reaction. The caustic pump is located in the basement of Building 10581. The 25% caustic solution (by weight) is added until the pH changes from below 1 to between 7.2 and 8.4. A pH of 7.5 is the ideal end point. Reaching this end point generally takes between 8 and 48 hours, depending on the quantity and concentrations of the initial chrome solution. Aqua -green slurry will form. Water may need to be added to keep the solution from solidifying and overloading or damaging the mixer.
When the pH has reached near 7.5, filtering may begin using one or both of the filter presses. The

filtrate is sampled to confirm proper removal of chrome metals.

Two batches of chromium, with an estimated total volume of 4,350 gallons of chrome solution, were treated and filtered. Chemical addition and total treatment time correspond fairly well to the initial concentrations. Batch 2 was larger and more concentrated in both hexavalent and total chrome, and required correspondingly higher quantities of sulfur dioxide, caustic, and filtering time.

Based on the estimated yearly quantities approaching 20,000 gallons of chrome solution, the system will likely require use of one filter press approximately 4 months per year. This filter press usage could be reduced further if cake discharges were performed more frequently. With the concentrated Batch 2, the filter press filled every 5 minutes but due to manpower limitations the cake was dropped much less frequently.

The chrome pretreatment process effectively removed both hexavalent and trivalent chrome. Initial chrome concentrations up to 5 percent solution (50,000 ppm) were effectively removed to below 20 ppm in the filtrate. Filtrate readings lower than 1 ppm are anticipated during normal operation.

The filter cake(sludge) has no free liquid and is 31% solids. The solids consist of 13% chromium oxide(in hydrated form), 8.5% phosphates, 4% other metals and 4.5% sulfates. In the first batch 7 drums of sludge were produced in 4 days and in the second batch 64 drums were produced in 30 days. As in the case of the cadmium sludge, this sludge is high in chromium content to make it feasible to recycle it. And this test demonstrated that the chromium in the concentrated solutions can be reduced from over 50,000 ppm to less than 20 ppm. Several lessons were learned which will be implemented to improve the equipment and procedures for the continuing pretreatment process.

PROVIDE DOCUMENTATION AND TRAIN

The implementation of these changes in the pretreatment process at the IWTP will require changes in procedures for the plant operators. A detailed and well organized Operation and Maintenance Manual was provided for their use. The operators were trained in the procedures as the project progressed and therefore know how to operate the new processes. The new manual will be a valuable training tool for new operators in the future.

RECYCLE NEW SLUDGES

Since the objective of the project was to reduce the disposal of hazardous waste sludge, the recycling of the two new sludges was investigated. They are clearly hazardous wastes. Vendors were found who professed the ability to recycle the sludges to reclaim the metal values so samples and profiles were provided to the two that appeared most promising. The selection process resulted in only one vendor who was capable of recycling both cadmium and chromium sludges and who met all the regulatory criteria. The selected vendor is U. S. Filter Recovery Services Inc., of Roseville, Minnesota. They treat the sludges by blending and drying, if necessary, to meet the feed stock specifications for the high temperature metal recovery(HTMR) process at Horsehead Resource Development Co. in Chicago. The flow chart in slide 23 illustrates the process. USEPA considers HTMR to be the best recovery option for metal bearing hydroxide sludge. One of the products produced by Horsehead , which utilizes the cadmium from our sludge, is lead/cadmium concentrate which is sold for further refinement and use in the manufacture of batteries and other products. Another of their products which utilizes the chromium is called Iron Rich Material(IRM). This product finds uses as kiln clinker necessary for the manufacture of cement and as an economical asphalt aggregate. Slide 24 illustrates the Horsehead process. The net result for Hill is that the cadmium and chromium are beneficially used and not disposed to landfill as a hazardous waste.

BENEFITS

The benefits of this project are summarized on slide 25. The cost to purchase, install and operate the equipment for the project was $100,000 which was provided from Pollution Prevention funds. No additional personnel were required for operation so no additional labor costs are assumed. Chemical usage is reduced. Since the cadmium solid is removed by filtration, it is not necessary to dissolve it by acid addition in the main plant. This saving in sulfuric acid usage was not measured during the project. Similar reductions in chemical usage were anticipated by treating the chrome concentrated solution rather than first diluting it with other wastewater streams. Quantifying the chemical savings was complicated by the fact that an upgrade of the IWTP main process came on-line in June 1997, simultaneously with the startup of the pretreatment separation process. Chemical savings observed are summarized in slide 26. It is likely that a large portion of the sulfur dioxide savings observed at the plant directly resulted from treating (reducing) a significant portion of the chrome in a concentrated batch rather than in a diluted form. An estimated $25,000 per year is saved in SO_2 usage with the pretreatment chrome separation process.

The main IWTP sludge volumes sent off site have decreased since July when the pretreatment process was initiated. Monthly values averaged above 28 tons per month prior to July 1997, and have averaged closer to 10 tons per month since then, or a 64% reduction. The reason has not been defined but it appears to be due to the pretreatment process changes. The current disposal cost is $0.21 per pound. This equates to an annual disposal cost of approximately $140,000 per year prior to installation of the filter presses. The reduction represents potential net savings of $91,000 per year for disposal of sludge from the IWTP main process.

Over the same six-month period, approximately 30,000 pounds of pretreatment sludge have been drummed and sent for recycle as mentioned previously. At a cost of approx. $0.50 per pound this equates to an approximate recycle cost of $30,000 per year.

The overall net savings in sludge disposal cost, therefore, is approx. $61,000 per year. This makes the total savings for chemical usage and sludge disposal approx. $86,000 per year.

The removal o f the cadmium and chromium in the pretreatment process may reduce the content of these metals in the final sludge such that it is no longer a characteristic hazardous waste. This is yet to be proven based on a more extensive mass balance study now underway. If this is the case and the F006 listed waste code can be removed as a result of other efforts now going forward the final sludge will no longer be a hazardous waste.

A less tangible but real benefit is the reduced liability resulting from recycling the sludges into useful products rather than placing them in hazardous waste landfills.

Another benefit of the project was a reduction in the cadmium content of the IWTP water effluent. It came at a very opportune time when the effluent standard had been reduced and without this project the limit would probably not have been achieved.

SUMMARY

The project demonstrated that cadmium and chromium can effectively be removed from the influent to the IWTP by minor changes in the pretreatment process. Removing these metals as solids and recycling them reduces the total sludge quantity and cost for disposal. Further, the final IWTP sludge may no longer be a characteristic hazardous waste. A rigorous mass balance study is now underway to determine the regulatory status of the sludge.

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